Small Marine Craft Emissions Observed during TexAQS II - 2006

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1. Introduction

A goal of the TexAQS II field campaign is to constrain emissions inventories for a number of biogenic and anthropogenic sources important to the study region by means of ambient measurement. Improved emissions inventories are a key tool in the development of abatement plans for air pollutants. Uncertainties in these inventories contribute a large portion to the total error for air quality and climate change modeling [IPCC, 2001].

The contribution of gasoline marine engines to the total anthropogenic VOC inventory for ozone non-attainment areas in the U.S. is significant [EPA, 1996]. The Houston-Galveston Bay (HGB) area is no exception; for the eight counties that make up the HGB region, marine recreational craft have been estimated to contribute 39% of the total volatile organic carbon (VOC) and 11% of carbon monoxide (CO) loading attributable to non-road sources [TCEQ, 2004].

NONROAD 2005 (v1.0), the current non-road mobile emissions modeling tool available from the EPA, provides both mass emission rates and emission factors for a large group of source categories, including marine recreational craft. TexAQS II provided a unique opportunity to compare ambient gas-phase mixing ratios of inorganic compounds attributable to small marine craft against this model; additionally, the importance of pleasure craft to anthropogenic VOC inventories is considered.

Recreation marine craft emission contribution for select U.S. cities, based on 1990 inventories (units % of total tons/summer day).

Non-attainment region	Rec. marine craft contribution to total anthro. VOC inventory
New York, NY	3.1 – 3.6
Philadelphia, PA	3.8 – 4.4
San Diego, CA	4.0 – 4.6
South Coast Basin, CA	3.5 – 4.0
Miami, FL	5.9 – 6.8
Milwaukee, WI	4.9 – 5.6

Estimated emission rates (tons/day) from marine recreational craft for the Houston-Galveston Bay area (8 counties). Percentage is the county emission rate attributed to marine recreational craft divided by the 8-county total emissions for all non-road mobile sources.

	VOC		NO_X		CO	
Brazoria	6.27	*7.7%*	0.45	*0.3%*	16.46	*2.2%*
Chambers	7.8	*9.6%*	0.58	*0.4%*	20.86	*2.8%*
Fort Bend	0.37	*0.5%*	0.02	*0.0%*	0.89	*0.1%*
Galveston	14.04	*17.2%*	1.03	*0.8%*	37.2	*4.9%*
Harris	1.54	*1.9%*	0.1	*0.1%*	3.89	*0.5%*
Liberty	0.55	*0.7%*	0.03	*0.0%*	1.33	*0.2%*
Montgomery	1.1	*1.3%*	0.07	*0.1%*	2.66	*0.4%*
Waller	0.16	*0.2%*	0.01	*0.0%*	0.38	*0.1%*
8 County Total	**31.83**	***39.0%***	**2.29**	***1.7%***	**83.67**	***11.1%***
All Non-Road	**81.64**		**136.74**		**755.8**	

2. Instrumental and Experimental

A subset of measurements made aboard the NOAA R/V Ronald H. Brown [RHB] by the NOAA Aeronomy Lab during the TexAQS II cruise are listed below.

Recreational marine craft were encountered throughout the campaign, especially when the RHB was cruising in Galveston or Matagorda Bay. To date, four days of the campaign have been surveyed for recreational marine craft plumes: 8/23, 9/2, 9/8 and 9/9. For these days, the author was stationed on the bow of the RHB to log encounters with the various craft.

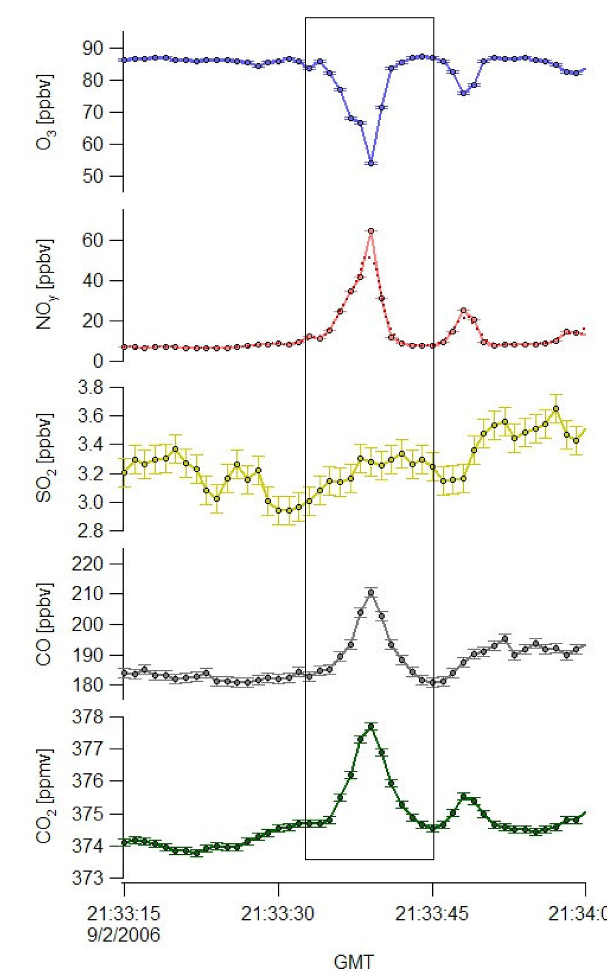
Further analysis of the remaining dataset will increase the size of the database compiled, although attribution of specific boat type will be limited.

Description of some of the gas-phase measurements made on RHB during TexAQS II and used in this work.

Analyte	Method	Uncertainty	Instrument Response
CO	Vacuum-UV resonance fluorescence	± (3% + 1.5 ppbv)	~ 0.5 Hz
CO_2	Non-dispersive IR	± 0.12 ppmv	~ 0.5 Hz
SO_2	UV-fluorescence	± (5% + 0.1 ppbv)	> 0.1 Hz
NO_y	Au-tube conversion (300 °C, H_2), followed by O_3-induced chemiluminescence	± (13% + 0.15 ppbv)	> 1 Hz
O_3	UV absorbance	± (3% + 0.4 ppbv)	> 0.1 Hz
O_3	NO-induced chemiluminescence	± (3% + 0.4 ppbv)	> 1 Hz

References
Carroll, J.N. and J.J. White, "Marine Gasoline Engine Testing", *SWRI Report 08.04017.11 & 03307*, 2001
Control of Air Pollution Emission Standards for New Nonroad Spark-Ignition Marine Engines, EPA Air and Radiation, 1996
Exhaust Emission Factors for Nonroad Engine Modeling--Spark-Ignition, *EPA Air and Radiation*, 2004
Gabele, P.A. and S.M. Pyle., Environ. Sci. Technol. 34 (3): 368-372, 2000
Gschwend P.M., et al., Environ. Sci. Technol. 16 (1): 31-38, 1982
IPCC, *Climate Change 2001: The Scientific Basis.* Intergovernmental Panel on Climate Change, 2001
Mace, B.E., et al., *SAE Paper 980681*, 1998

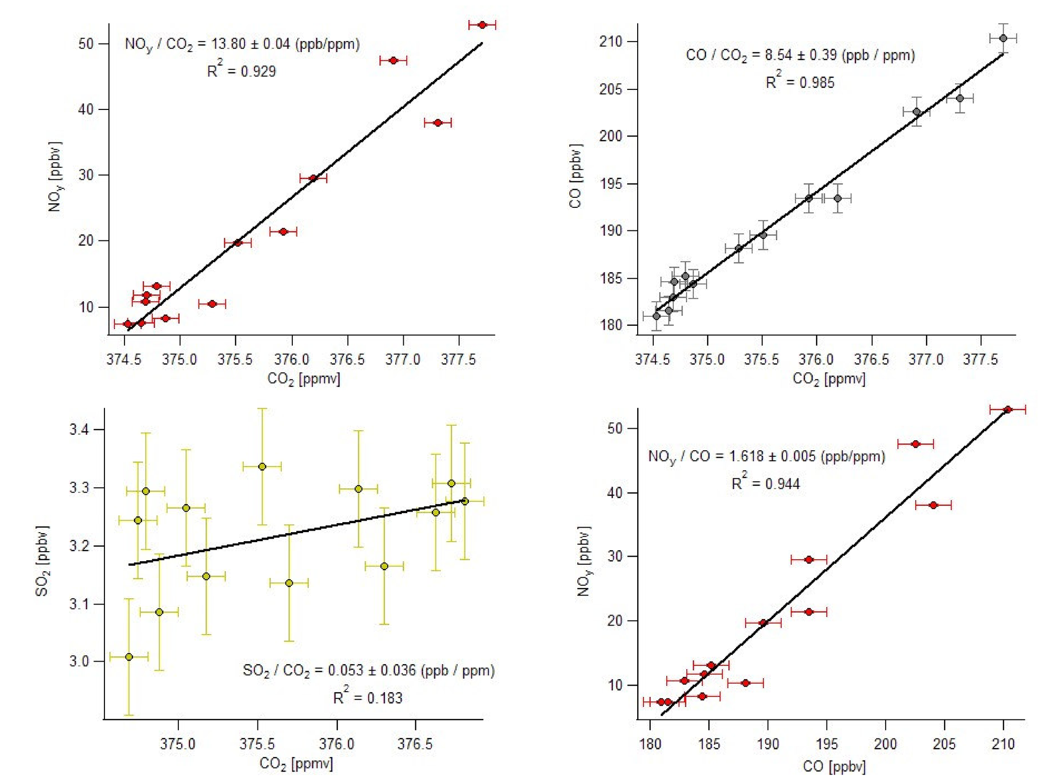
3. Individual Plume Analysis – An example



Time series plot of 1-second ambient mixing ratios of O_3, NO_y, SO_2, CO and CO_2, covering 45 seconds of data. Measurements made from the RHB while sailing out of Galveston Bay, near the inlet (red circle in Galveston Bay figure below)..

Dashed line on NO_y plot indicates 2-second averaging, used for linear fitting against CO and CO_2 data, due to differences in instrument response. NO_y, CO and CO_2 data are smoothed by 5-second average for comparison to SO_2 plumes (not shown).

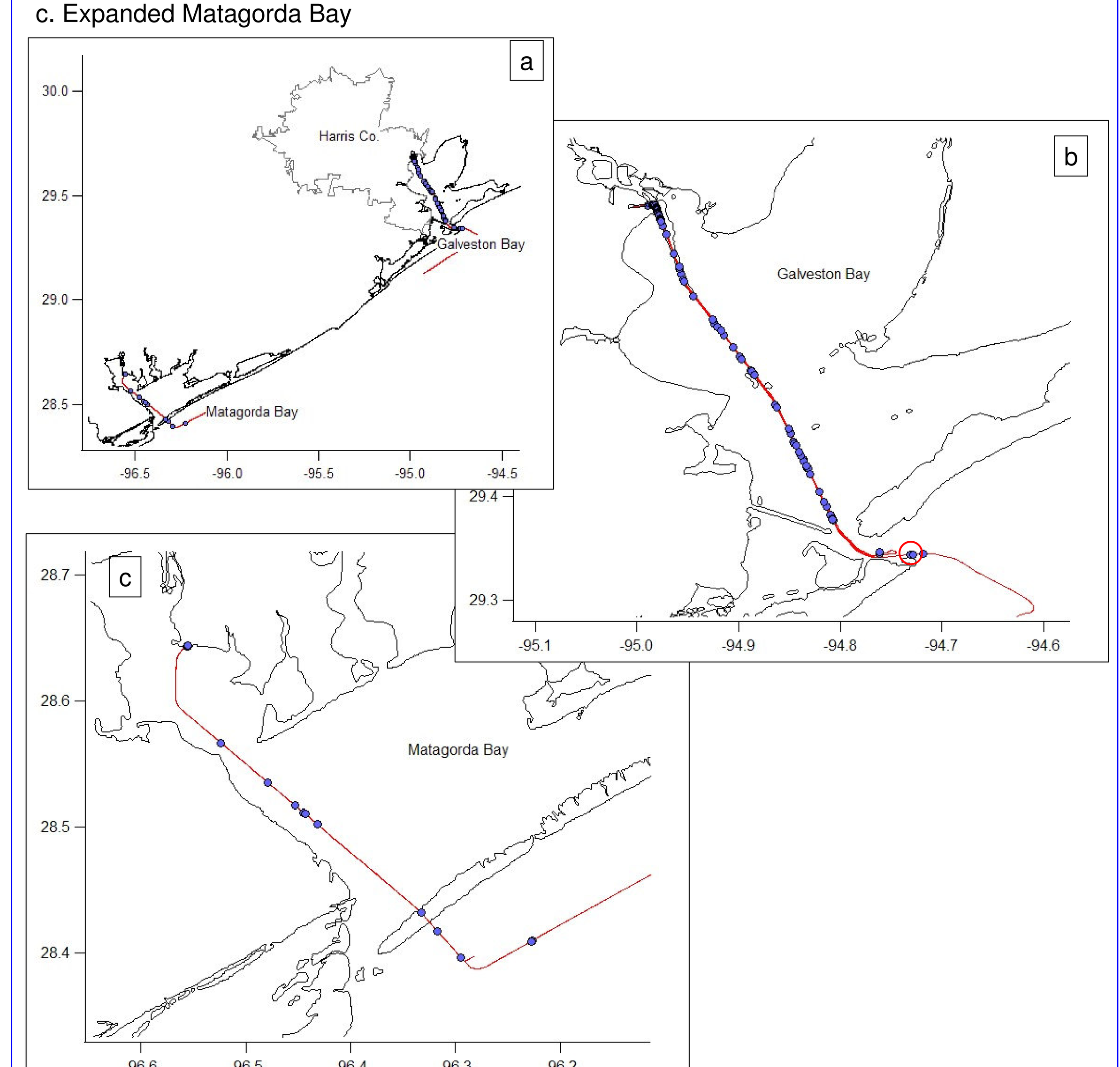
Molar emission ratios are derived from this plume via two methods – linear fitting of the 1-s data and integrating the area under the curve. The methods are comparable when the instrument time response is similar (e.g. CO & CO_2), but the linear fit appears biased for instruments with different response times. For this work, integrated area ratios are used, with a requirement of the linear fit $R^2 > 0.8$ used as a coarse filter (0.7 for SO_2 / CO_2).



Molar emission ratio (mol:mol)	Slope-derived	Integrated area-derived
NO_y / CO_2	13.8 (1.8) x10^{-3}	11.4 (2.0) x10^{-3}
SO_2 / CO_2	0.05 (0.04) x10^{-3}	0.09 (0.10) x10^{-3}
CO / CO_2	8.5 (0.5) x10^{-3}	8.8 (1.8) x10^{-3}
NO_y / CO	1.62 (0.65)	1.29 (0.28)

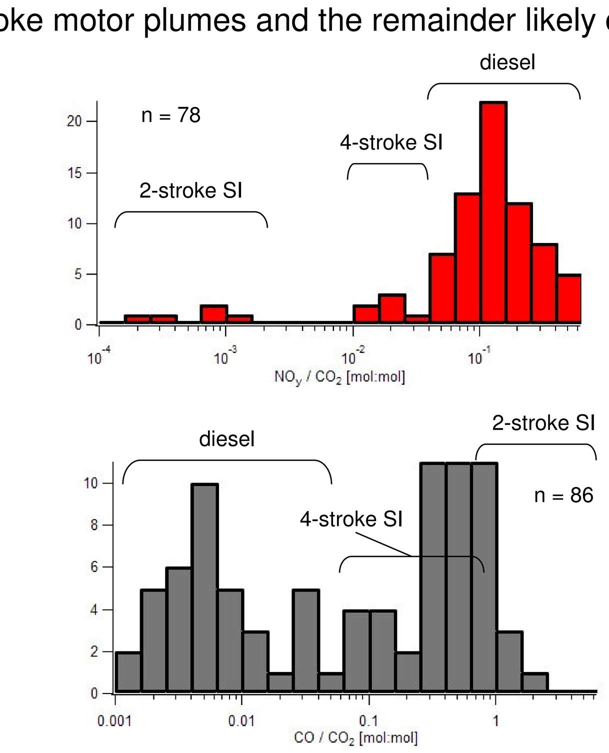
The four scatter plots (above right) show linear fits for the plume, using the data points within the box of the time-series plot. Error bars indicate instrument precision, used for the fits. Integrated areas were also calculated (not shown). The table (above left) shows the final molar emission ratios, with total instrument uncertainties used to estimate 1σ error for each value.

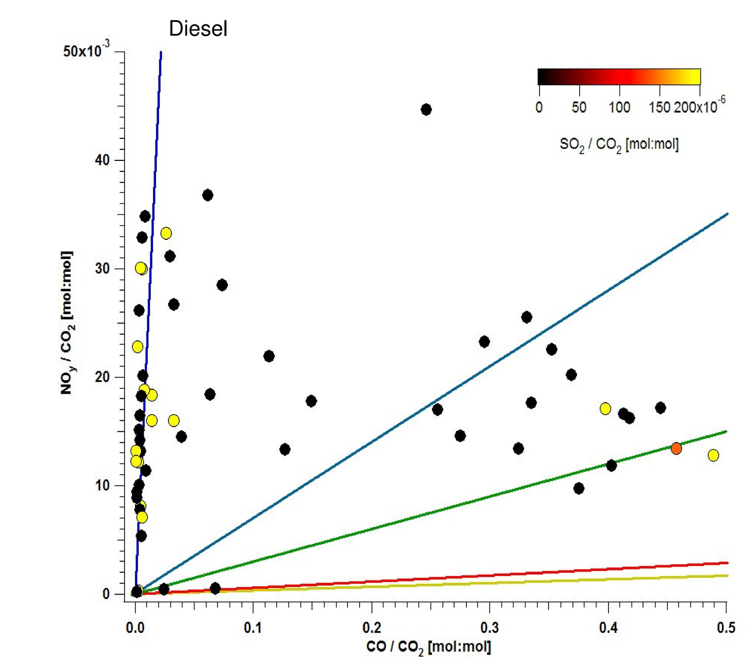
a. Overview map of TexAQS II study area. Red line indicates RHB ship track during the 4 data periods analyzed, blue circles show the location of the RHB during a plume encounter.
b. Expanded Galveston Bay; red circle shows location of example plume.
c. Expanded Matagorda Bay



4. Results for TexAQS II

To date, a total of 111 plumes have been analyzed for the TexAQS II dataset. Histograms for the NO_y / CO_2 and CO / CO_2 molar emission ratios are show below. The majority of the plumes well-characterized by NO_y / CO_2 appear from diesel engines, rather than the gasoline-powered (SI) motors that were targeted. The CO / CO_2 distribution has eight more plumes, all likely SI where NO_y / CO_2 correlations were poor. A scatter plot of the two ratios indicates only 3 plumes which could be classified as 2-stroke engines for the data set, with ~20 modern 4-stroke motor plumes and the remainder likely diesel.



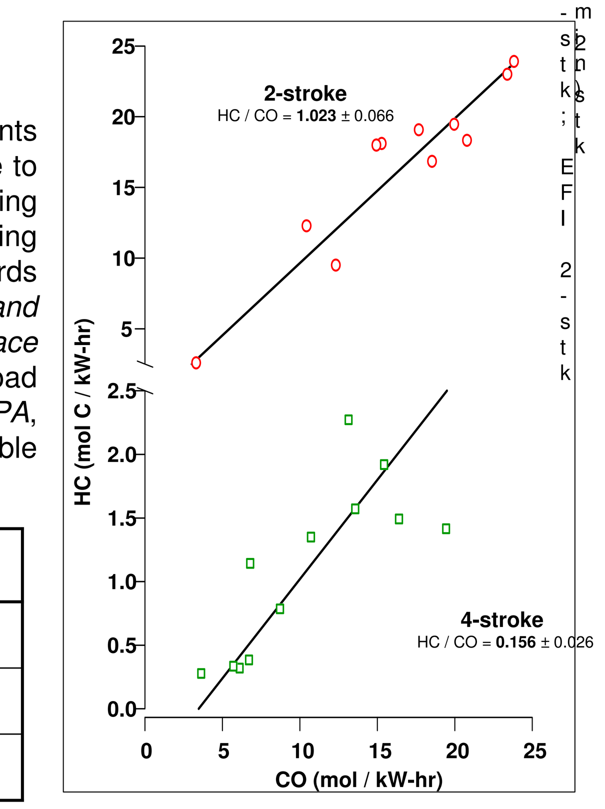


5. Estimating VOC output from CO

VOC instruments aboard the RHB were generally unable to provide measurements of VOC emissions in small marine craft exhaust plumes. However, it is possible to estimate hydrocarbon (HC) emissions from HC / CO ratios calculated from existing data. There are several published studies of marine engine emissions, surveying carbureted 2-stroke outboard engines (9-30 HP), carbureted 4-stroke outboards and both carbureted and fuel-injected 4-stroke inboards (8-300 HP) [*Zinger and Hecker*, 1979; *Juttner et al.*, 1995; *Samulski*, 1996; *Barton and Fearn*, 1997; *Mace et al.*, 1998; *Gabele and Pyle*, 2000; *Carroll and White*, 2001]. The EPA NonRoad 2005 model has several classes of marine engines, summarized below [*EPA*, 2005]. The HC/CO emission ratios used in the model agree well with available literature data.

Engine Type / Control Tech.	HC/CO (mol:mol)	Engine Type / Control Tech.	HC/CO (mol:mol)
2-stk outboard, M1 Tech pre-controlled	**0.82 – 1.30**	4-stk outboard, M4 Tech pre-controlled	**0.057 – 0.10**
2-stk outboard, M8 Tech electronic fuel injection	**0.15 – 0.20**	4-stk inboard, M3 Tech pre-controlled	**0.076**
2-stk outboard, M9 Tech direct fuel injection	**0.22 – 0.34**	4-stk inboard, M10 Tech electronic fuel injection	**0.084**

Derived HC / CO emission ratios for various marine engine classes. Values listed give range across engine power classifications greater than 3 HP.



Published hydrocarbon emission rate vs. carbon monoxide emission rates. Circles represent carbureted 2-stroke outboard marine engines, squares represent IB/OB 4-stroke marine engines. Correlations determined by reduced major-axis regression.

6. Conclusions

- 111 potential small marine craft exhaust plumes measured during TexAQS II have been analyzed to date; only 3 of these plumes are characteristic of 2-stroke gasoline engines. Recognizing an inherent sampling bias due to the limited operating area accessible to the RHB, this indicates that the current inventory of recreational marine craft used by NONROAD 2005 may be incorrectly skewed toward these engine types, thereby attributing too high emissions of VOCs to this class.
- There were approximately twenty 4-stroke gasoline engine plumes identified to date. All show emission ratios characteristic of modern, electronic fuel injected engines, rather than less efficient carbureted motors.
- The majority of the exhaust plumes are characteristic of diesel engines. Since plumes from all large vessels, as identified by a Marine Automated Identification System, were culled from the database, this may indicate that small commercial fishing boats (trawlers) are a significant pollution source in Matagorda and Galveston Bays. A subset of these exhaust plumes had higher than expected CO/CO_2 emissions.
- Further work includes: processing of the entire database (6+ weeks) to identify more exhaust plumes, and the use of high resolution formaldehyde, ethylene and light-absorbing carbon data to assess emissions of these species.

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Photo of small marine craft courtesy of D. Welsh-Bon.

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